PATENT ABSTRACTS OF JAPAN

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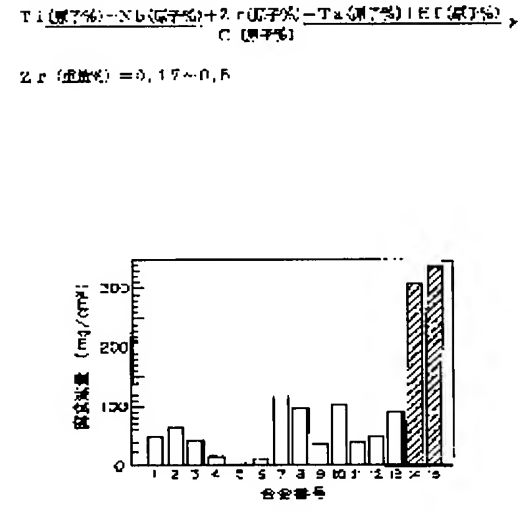
(54) HIGH CORROSION RESISTANT COBALT BASE ALLOY



(57)Abstract:
PROBLEM TO BE SOLVED: To produce a Co base super alloy improved in high temp. corrosion resistance without deteriorating its creep rupture strength as the material suitable for high temp. parts for a high efficiency gas turbine.
SOLUTION: This alloy has a compsn. contg., by weight, 23 to 27% Cr, 0.05 to 0.45% C, 9.5 to 11.5% Ni, 5 to 10% W, 0.005 to 0.05% B, ≤1% Si, ≤1% Mn, ≤2% Fe, ≤1% Al, 2 to 5 elements among the groups of MC carbide forming elements composed of Zr, Nb, Ti, Ta and Hf, and the balance cobalt with inevitable impurities, and in which, among the groups of MC carbide forming elements, 0.2 to 1% Zr and 0.05 to 0.15% Nb are contained as essential components, and, moreover, each MC carbide forming element is contained so as to satisfy the following formula: Ti(atomic %)+Nb(atomic %)+Zr(atomic %)+Ta(atomic %)+Hf(atomic %)/ C(atomic %)×Zr(wt.%)=0.17 to 0.5.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to Co radical alloy excellent in corrosion resistance, especially relates to Co radical superalloy suitable as an ingredient of the elevated-temperature components for gas turbines.
[0002]
[Description of the Prior Art] Co radical superalloy is widely used as the nozzle (stationary blade) of an industrial gas turbine, and a charge of elevated-temperature components material of a combustor. However, in order to apply to the efficient gas turbine which raised the temperature of combustion to which development is advanced in recent years, it is difficult to fill the demand to corrosion resistance with the high intensity Co radical superalloy by the conventional technique.
[0003] As Co radical superalloy for gas turbines, there are some which were indicated by official reports, such as JP,61-56304,B, JP,62-49344,B, and JP,4-59378,B.
[0004]
[Problem(s) to be Solved by the Invention] Since a problem is in elevated-temperature corrosion resistance when application to an efficient gas turbine with the high temperature of combustion is assumed, Co radical superalloy in the conventional technique has the indispensable surface coating for corrosion prevention. However, if coating exfoliation occurs during system use, when the corrosion resistance of a base material alloy is not enough, corrosion advances accelarative and construction of these coatings not only leads to the rise of a manufacturing cost, but may do the serious damage for a product. For this reason, the efforts for for the corrosion-resistant improvement in an alloy have accomplished in every direction. However, the technique of the corrosion-resistant improvement in the conventional technique of the increment in Cr addition has already come to the limitation, and development of the corrosion-resistant new improvement technique was needed, for example.
[0005] The purpose of this invention is based on these to offer the elevated-temperature components for efficient gas turbines using Co radical alloy and this alloy which raised elevated-temperature corrosion resistance, without spoiling creep rupture strength.
[0006]
[Means for Solving the Problem] Co radical superalloy concerning this invention adds amelioration to the conventional technique about the following points, in order to attain the above-mentioned purpose.
[0007] It is said that the thing most important generally as a factor which influences the corrosion resistance of an alloy is Cr content in an alloy matrix. Then, also in development of Co radical superalloy, it has been made good in the range which does not have a bad influence on many of other properties to make Cr addition increase as much as possible. For this reason, in Co radical superalloy for industrial gas turbine nozzles with the high demand to corrosion resistance, 27 - 29% of Cr is usually added. With this kind of alloy, addition of 30% or more of Cr is made not desirable from the point of phase stability, and Cr addition of said conventional material is close to a limitation. Moreover, although corrosion resistance improves also by reducing C addition, since high temperature strength falls to coincidence remarkably, it cannot but grow into that to which the application was limited.
[0008] However, by this invention persons' adjusting the amount of Cr(s) lowness rather, and carrying out minute amount compound addition of the suitable MC carbide formation element In order to make that the elevated-temperature corrosion resistance superior to the conventional material is acquired, and such high corrosion resistance discover, while the amount of C was limited to 0.05 - 0.45% of range, it studied that two sorts, Zr and Nb, had to

be added at least among MC carbide formation elements.
[0009] Moreover, such high corrosion resistance found out that outstanding Co radical superalloy which is enough maintained even if it carries out minute amount addition of Ta, Ti, and the Hf as a MC carbide formation element for the improvement in high temperature strength in addition to Zr and Nb, therefore combines high intensity and high corrosion resistance was obtained.
[0010] Furthermore, this invention persons improve the formula which should serve as MC carbide formation element indicated by JP,61-56304,B and an index of addition balance optimization of C, and are formula (1) [0011] of a degree.
[Equation 3]

$$\frac{Ti(\text{原子\%})+Nb(\text{原子\%})+Zr(\text{原子\%})+Ta(\text{原子\%})+Hf(\text{原子\%})}{C(\text{原子\%})} \times Zr(\text{重量\%}) \quad \cdots\cdots (1)$$

[0012] It found out that the optimal property was acquired by controlling the value calculated as be alike in the range of 0.17-0.5.
[0013] The high corrosion resistance Co radical alloy of this invention by weight Cr:23-27%, C:0.05 - 0.45%, nickel: 9.5-11.5%, W:5 - 10%, B:0.005 - 0.05%, Si: Less than [1%], less than [Mn:1%], less than [Fe:2%], less than [aluminum:1%], Two to 5 element of the MC carbide formation element groups which consist of Zr, Nb, Ti, Ta, and Hf, It consists of cobalt and an unescapable impurity. Among MC carbide formation element groups further Remainder : Zr:0.2-1%, It is what makes Nb:0.05-0.15% indispensable and is characterized by controlling each MC carbide formation element by the value calculated by the above-mentioned formula (1) in the range of 0.17-0.5. It is suitable for the elevated-temperature components for industrial gas turbines with which especially the outstanding elevated-temperature corrosion resistance is demanded, for example, combustor components.
[0014] High corrosion resistance Co radical alloy with still more nearly another this invention by weight Cr:23-27%, C:0.2 - 0.45%, nickel:9.5-11.5%, W:5 - 10%, B:0.005 - 0.05%, less than [Si:1%], less than [Mn:1%], less than [Fe:2%], aluminum: Less than [0.1%], Zr:0.2-0.7%, Nb:0.05-0.15%, Ta:0-0.44%, Ti:0.1-0.4%, Hf:0-1%, the remainder : It is what consists of cobalt and an unescapable impurity. However, made three elements of Zr, Nb, and Ti indispensable among MC carbide formation elements of Zr, Nb, Ta, Ti, and Hf, Ta and Hf were made to contain alternatively, and it controls by the value calculated by the above-mentioned formula (1) in the range of 0.17-0.5. This alloy fits the elevated-temperature components for industrial gas turbines of which high high temperature strength is required with elevated-temperature corrosion resistance, for example, the nozzle for gas turbines.
[0015]
[Function] An operation of each element which constitutes the high corrosion resistance Co radical superalloy of this invention is shown below. Cr(s) are main elements which form a precise oxide coat in an alloy front face under an elevated temperature, and boil and twist the corrosion resistance of an alloy. Therefore, in the corrosive environment to which the elevated-temperature components of an industrial gas turbine are exposed, 20% or more of addition is indispensable. However, 30% or more of addition spoils the phase stability of an alloy host phase. Moreover, while Cr combines with C, and forms a lot of chromium carbide in coincidence and detailed thing about 0.5 micrometers or less contributes to improvement in high temperature strength among those, a big and rough thing is further made condensation big and rough under an elevated temperature, and has a bad influence on reinforcement and corrosion resistance both. If Cr should limit the addition to 23 - 27% of range in this invention alloy, and sufficient corrosion resistance is not acquired at less than 23% by the dissolution Cr concentration fall in an alloy host phase and it exceeds 27% from the above thing, increase of

the amount of deposits of big and rough chromium carbide will become a cause, and high corrosion resistance [as / in this invention] will not be discovered too.
[0016] C forms chromium carbide as above-mentioned, and also forms stable MC carbide with MC carbide formation elements, such as Zr, Nb, Ta, Ti, and Hf, and an among these sufficiently detailed thing has the remarkable effectiveness of raising high temperature strength including creep rupture strength. For this reason, in order for reinforcement to improve with the increment in C addition and to maintain the high intensity in this invention alloy generally, 0.05% or more needs to be added. However, in order for corrosion resistance to tend to deteriorate conversely and to realize high corrosion resistance in this invention with the increment in the amount of carbide deposits, it may be necessary to be 0.45% or less. Moreover, when applying to the gas turbine as which high high temperature strength is required especially, it should consider as 0.2 - 0.45% under suitable addition of MC carbide formation element group described later.
[0017] Each of Zr, Nb, Ta, Ti, and Hf(s) has high carbide organization potency, and since the generated carbide serves as MC mold, they is called MC carbide formation element. Among MC carbide, an object with a particle size of 1 micrometers or more divides chromium carbide with the inclination to follow a grain boundary and a dendrite boundary and to deposit, and a detailed object controls big and rough-ization of the chromium carbide under an elevated temperature, while contributing to the improvement in on the strength. According to a fragmentation operation of this big and rough chromium carbide, while the ductility fall under elevated-temperature long duration use is suppressed, the remarkable corrosion-resistant improvement effectiveness in this invention is acquired. However, since these element groups not only cause corrosion resistance aggravation depending on superfluous addition, but a high-temperature-strength property gets worse, the addition must be examined carefully.
[0018] Since an improvement operation of high temperature strength and the chromium carbide fragmentation operation of especially Nb are very high, 0.05% or more of addition is indispensable, but if it exceeds 0.15%, since corrosion-resistant aggravation is remarkable, an addition will be limited to 0.05 - 0.15% of range.
[0019] In order to acquire the high corrosion resistance in this invention with the outstanding carbide fragmentation operation, it becomes indispensable adding Zr, but unlike Nb, corrosion resistance will not be spoiled if it is 1% or less of addition. Moreover, since it has the outstanding grain boundary potentiation and there is the remarkable improvement effectiveness in ductility, the ductility fall by high-intensity-izing can be prevented. However, since these effective operations are not acquired depending on less than 0.2% of addition, they must be added by 0.2 - 1% of within the limits. Moreover, since the inclination which promotes pervasion of the grain boundary a little by addition exceeding 0.7% is seen when applying to the application put to the bottom of elevated-temperature quantity stress for a long time, considering as 0.2 - 0.7% is desirable. (Zr/Nb) As for a ratio, 1-10 are desirable, and 2-7 are more desirable.
[0020] About Ti, Ta, and Hf, even if it does not add this, the high corrosion resistance in this invention and the reinforcement in a general application are fully secured. However, when very high high temperature strength is required of corrosion resistance and coincidence (for example, when application to a gas turbine nozzle is considered), only by Nb and Zr, MC carbide potentiation is not enough and it becomes indispensable adding [of these element groups] it.
[0021] Although 0.1% of addition of Ti was indispensable because of the improvement in high temperature strength, if it exceeds 0.4%, in order to have a bad influence on fluidity, it considered as 0.1 - 0.4% of range. (Ti/Nb) As for a ratio, 1-6 are desirable, and 2-4.5 are more desirable.

[0022] If it is less than [Ta:0.44%] and less than [Hf:1%] about Ta and Hf, the adoption or rejection of the addition is the range of discretion of a manufacturer. To a thing with an improvement operation of high temperature strength especially strong [Ta], Hf is effective in contributing also to strengthening of the grain boundary and raising the creep strength under low stress, and elevated-temperature ductility, and the optimal alloy is obtained by adjusting an addition according to the property searched for with the application object of this alloy. However, when it adds exceeding Ta:0.44% and Hf:1%, corrosion resistance aggravation is remarkable and it is desirable to consider as less than [Ta:0.3%] and less than [Hf:0.5%] for the applications as which high corrosion resistance is required especially.
[0023] Furthermore, the total amount of the addition of these MCs carbide formation element group has the optimal range in balance with C addition. Then, it is a degree type [0024] about such balance.
[Equation 4]

$$\frac{\text{Ti(原子\%)}+\text{Nb(原子\%)}+\text{Zr(原子\%)}+\text{Ta(原子\%)}+\text{Hf(原子\%)}}{\text{C (原子\%)}} \times \text{Zr (重量\%)}$$

[0025] When it was evaluated as alike and the value of a formula was in the range of 0.17-0.5, it became clear that the outstanding property in this invention was acquired. Therefore, the addition of MC carbide formation element group must be adjusted so that the value calculated by the upper type may not deviate from the range of 0.17-0.5.
[0026] Although aluminum is effective in forming a precise alumina coat in an alloy front face, and raising corrosion resistance under a super-elevated temperature 950 degrees C or more, a stable coat is not not only formed, but below 950 degrees C, it worsens corrosion resistance conversely. Moreover, if it is easy to make inclusion harmful at the time of coagulation and adds exceeding 1%, fluidity and weldability will be degraded and it will have a bad influence also on high temperature strength. Therefore, although 1% or less of addition is permitted on the assumption that use at 950 degrees C or more, considering as 0.1% or less is more desirable.
[0027] nickel is added for phase stability maintenance of an alloy host phase, and 9.5 - 11.5% of addition makes phase stability the highest.
[0028] Although added 5% or more as a solid-solution-strengthening element, since the deposit of a harmful phase would take place under an elevated temperature if 10% is exceeded, W could be 5 - 10%.
[0029] Although it was added as a crystal-stressing element and B raised elevated-temperature ductility, at 0.005% or less, it was ineffective, and if 0.05% is exceeded, in order to cause embrittlement of a grain boundary conversely, it could be 0.005 - 0.05%.
[0030] Although conventionally added as a deoxidizer at the time of the dissolution, it is not necessary to add Si and Mn positively by current by advance of a vacuum melting technique. Moreover, if Si and Mn are added exceeding 1%, in order to form inclusion harmful at the time of casting and to reduce reinforcement, when these elements need to be added, both elements must be made into 1% or less for convenience' sake on manufacture. 0.05 - 0.25% of especially Si is desirable.
[0031] Fe is effective in raising the yield of these light elements by producing a dissolution raw material as Fe alloys, such as Fe-C and Fe-B, on the occasion of addition of C, B, etc. However, since high temperature strength is reduced depending on addition exceeding 2%, it should consider as 2% or less. 0.05 - 0.3% is especially desirable.
[0032]
[Embodiment of the Invention] Hereafter, the gestalt of operation explains the high corrosion resistance Co radical superalloy of this invention.

(Gestalt 1 of operation)
[0033]
[Table 1]

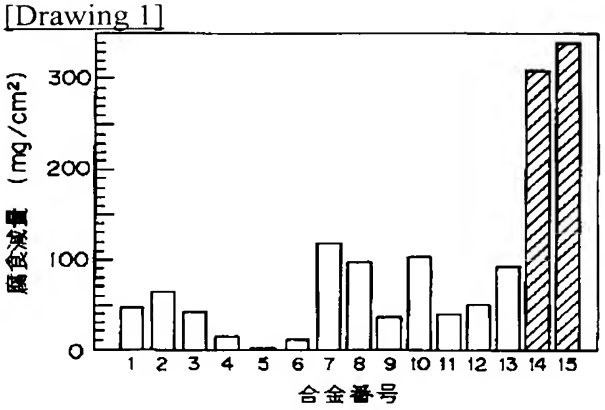
	合金No.	C	Cr	Ni	W	Nb	Zr	Ti	B	Al	Ta	Hf	Si	Mn	Fe	Co	(M/C)×Zr	Ti/Nb	Zr/Nb	Mn/Si
本発明合金	1	0.22	25.4	10.5	7.4	0.14	0.29	0.30	0.014	—	—	—	0.09	0.41	0.12	Bal.	0.173	2.14	2.07	4.56
	2	0.34	25.5	10.5	7.3	0.13	0.45	0.28	0.018	—	0.42	—	0.11	0.44	0.16	Bal.	0.230	2.15	3.46	4.00
	3	0.27	25.1	10.4	7.4	0.12	0.58	0.27	0.015	—	—	—	0.15	0.38	0.14	Bal.	0.343	2.25	4.83	2.53
	4	0.25	24.9	10.4	7.5	0.11	0.52	—	0.015	—	—	—	0.14	0.41	0.17	Bal.	0.172	0	4.73	2.93
	5	0.07	24.7	10.5	7.4	0.12	0.29	0.25	0.013	—	—	—	0.09	0.38	0.10	Bal.	0.482	2.08	2.42	4.22
	6	0.17	25.2	11.1	7.2	0.10	0.31	0.25	0.016	—	—	—	0.09	0.45	0.09	Bal.	0.212	2.50	3.10	5.00
	7	0.26	25.2	10.0	7.6	0.09	0.36	0.28	0.015	0.50	—	—	0.14	0.43	0.15	Bal.	0.179	3.11	4.00	3.07
	8	0.23	26.6	9.9	7.3	0.08	0.42	0.29	0.007	—	—	—	0.13	0.42	0.16	Bal.	0.253	3.63	5.25	3.23
	9	0.26	25.4	9.9	7.7	0.10	0.33	0.28	0.009	0.08	0.15	—	0.08	0.47	0.20	Bal.	0.173	2.80	3.30	5.88
	10	0.41	25.2	9.9	7.7	0.09	0.52	0.28	0.012	0.10	0.33	—	0.10	0.39	0.12	Bal.	0.218	3.63	5.78	3.90
	11	0.30	25.2	10.0	7.5	0.07	0.48	0.29	0.008	—	0.32	—	0.11	0.41	0.18	Bal.	0.266	4.14	6.86	3.73
	12	0.33	25.3	10.1	7.5	0.09	0.41	0.25	0.008	—	0.26	0.35	0.10	0.33	0.18	Bal.	0.210	2.78	4.56	3.30
	13	0.24	23.5	10.2	7.4	0.10	0.40	0.28	0.009	—	—	—	0.12	0.40	0.22	Bal.	0.226	2.80	4.00	3.33
比較合金	14	0.22	29.5	10.6	7.1	—	—	—	—	—	—	—	0.15	0.42	0.13	Bal.	0	—	—	2.80
	15	0.37	29.5	9.8	7.0	0.27	0.18	0.15	0.009	—	—	—	0.09	0.41	0.15	Bal.	0.047	0.56	0.67	4.51

[0034] Table 1 shows the chemical composition (% of the weight) of the main sample offering alloys. No.1-13 -- this invention alloy -- it is -- No. -- 14 and 15 are comparison alloys. Each comparison alloy is Co radical superalloy, and has a presentation equivalent to an ingredient [finishing / application on the elevated-temperature components of the gas turbine marketed].
[0035] Ingot making of these alloys was carried out with the vacuum RF fusion furnace, they produced the test piece by machining after precision casting and heat treatment, and presented the evaluation trial with it.
[0036] Drawing 1 shows the fused salt corrosion test result of a sample offering alloy. after being immersed into the sodium-sulfate-sodium chloride mixed salt which 3:1 came out of the sample offering alloy comparatively by the weight ratio, and was mixed and performing 900 degrees C and heating of 100 hours, descaling is carried out, the corrosion weight loss of this invention alloy which carried out weighing capacity and calculated loss in quantity by corrosion is 1/2 or less [of a comparison alloy], and the corrosion resistance in this invention which was very excellent is shown.
[0037] Drawing 2 shows 850 degrees C of creep rupture time of 2 13 kgf/mm. Also in No.5 with the lowest reinforcement, reinforcement equivalent to a comparison alloy is obtained among this invention alloy, and also high intensity and coexistence of high corrosion resistance are attained with the alloy of No.2 which thought high temperature strength as important, and 10 grades.
[0038] (Gestalt 2 of operation) The nozzle for gas turbines shown in drawing 3 was manufactured using the alloy of No.11 shown in Table 1 of the gestalt 1 of operation. As shown in drawing, a vane 3 is formed between the outside sidewall 1 and the inside sidewall 2 at one, a vane 3 has the hollow structure 4 for the need for air quenching from an inside, and many cooling holes 5 used as a cooling air outlet are formed in a vane 3 and sidewalls 1 and 2. Although the vane 3 was one thing, a 2piece, a 3piece, a 4piece or five pieces, and plurality should be united.

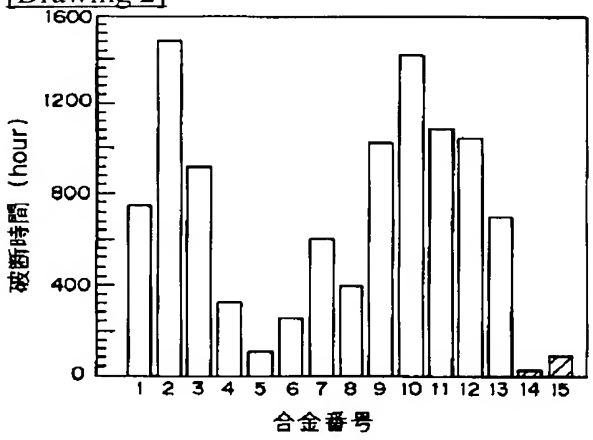
[0039] However, the gestalt of this operation connects two or more nozzles of the configuration shown in drawing 3 from the request on the manufacture on a gas turbine body design, and cast as one, the hollow structure for cooling is omitted, or it does not restrict changing the number and location of a cooling hole. Moreover, it is possible to construct suitable corrosion-resistant coating for a vane and a sidewall or thermal shield coating according to the environment to be used, and to aim at further improvement in various properties. Moreover, in that case, the corrosion resistance which was excellent in this invention alloy can prevent accelarative advance of the corrosion accompanying the coating exfoliation system in use stated by the term of the technical problem of said invention, and can secure the dependability of a product.
[0040] If in charge of manufacture of this nozzle, it is suitable to be based on the vacuum precision casting using a lost wax process, and the nozzle which has complicated hollow structure in a vane by this was obtained below by the minimum casting defect incidence rate permitted as a product. Moreover, heat treatment adjusted the organization like the gestalt 1 of operation.
[0041]
[Effect of the Invention] According to this invention, without [without it spoils the dependability of each part article by obtaining Co radical alloy which has the elevated-temperature corrosion resistance which was conventionally superior to the alloy, and high temperature strength, and applying this Co radical alloy to the elevated-temperature components of a gas turbine, especially a gas turbine nozzle and the components for combustors, or] causing the rise of a manufacturing cost in vain, elevated-temperature-ization of the temperature of combustion is attained and the gas turbine of efficient high-reliability can be manufactured.

DRAWINGS

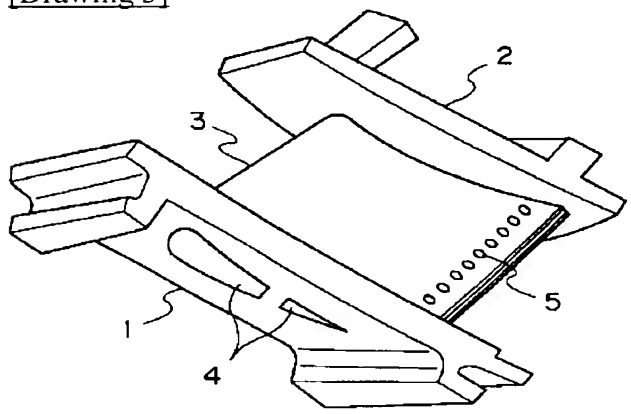
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]